THE INFLUENCE OF THE PRODUCTS OF COMBUSTION OF SULFUR-CONTAINING FUEL DISTILLATES ON THE CONSTRUCTION MATERIALS OF GAS TURBINES

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From obtained laboratory data recommendations have been made about experimenting with sulfur-containing diesel fuels in natural gas-turbine plants. The results of these experiments have confirmed the correctness of the laboratory experiments and shown the suitability of sulfur-containing diesel fuel for reliable operation of gas turbine plants.

The seven-year plan for the development of the national economy foresaw the considerable growth in the capacity of gas turbine power installations in industry and transportation. A substantial part of them will work on sulfur-containing fuel and, considering the prospects for the development of the oil industry, this will be fuel containing ~1.0% of sulfur. In this connection questions dealing with the corrosive action of fuel combustion products on components of the steam-passing parts of the turbine acquire especial significance.

The corrosive properties of sulfur oxides formed in the combustion

of sulfur compounds contained in the fuel may, in respect to metals, appear under two essentially different conditions: At low and at high temperatures. In the first case an electrochemical (acid) corrosion, and in the second a chemical (gaseous) corrosion is observed.

The problem of low-temperature corrosion in gas turbines has as a rule no great significance because of the high temperature of the gases on exhaust, although at times of starting and stopping, and also when using exhaust gases, low temperature corrosion may also take place.

The greatest danger connected with the presence sulfur-containing cases, sulfuric anhydride, and sufficient amounts of oxygen (resulting from the great excess of air during combustion) is in the combustion products in the high-temperature chemical corrosion of the elements of the gas turbine. High temperatures and the considerable bathing rates of the components on the part of combustion products create conditions in which corrosion becomes more intense.

The corrosion resistance of the metals in the gas tract of gas turbine units in the presence of combustion products of sulfur-containing fuels has not yet been studied sufficiently.

Below are listed the experimental results of the corrosive action of the combustion products of sulfur-containing diesel fuel on metals used in gas turbine construction, obtained in a small laboratory combustion chamber in which were placed specimens prepared from sheet, plate, and the working blades of gas turbines.

Diesel fuels containing from 0.2 to 1.6% sulfur were tested (Table 1). Our standard was the low-sulfur diesel fuel DS, GOST* 4749-49 (0.2% S), currently used in gas turbines.

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*GOST = All-Union State Standard.

Corrosion was evaluated by weighing the specimens before and after the tests. Before weighing the plates after the experiments, they were first subjected for 2-3 minutes to electrochemical treatment in a fusion of 40% Na_2CO_3 and 60% NaOH at 500-550°C and a current of 0.25 amp/cm².

In the first series of experiments the corrosion resistance of an alloy under the influence of sulfur-containing fuel combustion products was studied. In this the metal specimens were subjected to the action of combustion products for separate 10-hour stages, in the intervals between which the specimens were transferred from the experimental box into a desiccator which excluded the condensation of air moisture on their surfaces.

Table 1

Physicochemical Constants of Diesel Fuels

Constants	DS, GOST 4749-49	S-containing fuel from the Novo-Kuibyshev factory GOST 305-58	Experimental sulfur-containing fuels from the factories in		
			Lyubertsy	Novo-Kuibyshev	Ufa
Sulfur, %	0.2	0.99	1.4	1.57	1.6
Chemical composition of hydrocarbons, %...					
Naphthenes and paraffins	84.9	74.4	62.6	82.0	70.5
Aromatics	15.1	25.6	37.4	18.0	29.5
Ash, %	Absent		0.017	0.0027	Absent
Fractional composition					
Start of boiling, °C	232	–	200	187	–
10% Boils away at °C	250	247	251	217	225
50% Boils away at °C	278	271	288	250	271
90% Boils away at °C	318	314	329	305	331
96% Boils away at °C	300	334	346	334	365
Viscosity, 20°C, stoke	2.5	4.9	6.94	2.06	4.97

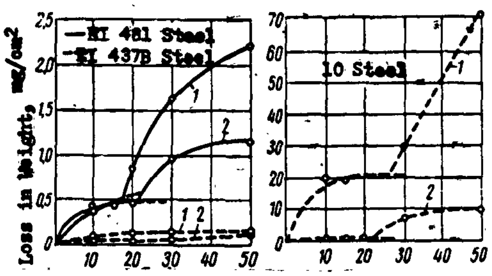

Fig. 1. Kinetics of Steel Corrosion in Diesel Fuel Combustion Products at 650°C.
1) DS, GOST 4749-49 (0.2% S). 2) Experimental sulfur-containing fuel (1.4% S).

Figure 1 gives the kinetics of corrosion of steels on an iron (EI 481) and a nickel (EI347B) base in the combustion products of sulfur-containing fuel (1.4% S) and the standard fuel (0.2%) in comparison with ordinary steel (10 Steel) after 50 hours at 650°.

From the data shown it can be seen that the nickel alloy hardly corrodes at all at the given temperature; but the alloy on an iron base corrodes substantially; 10 Steel is especially sensitive to gaseous corrosion, losing 30-40 times more weight in 50 hours than EI481 steel.

A peculiarity of the corrosion of steels on an iron base is that raising* the sulfur content in the fuel lowers the corrosion rate. It is obvious that under the influence of fuel combustion products containing sulfur, the surface of these steels can quickly develop a protective film that retards corrosion.

These facts are confirmed by the results of tests to determine the corrosion resistance of another steel on an iron base — 2Kh13— in the combustion products of fuels containing different percentages of sulfur (Fig. 2).

After 10 hours at 750° in low-sulfur fuel, plate scorching was obtained. Testing specimens of this steel at the same temperature in sulfur-containing fuels (1.0 and 1.57% S) did not result in such scorching.

The corrosion of nickel alloy EI437B at 950° increases somewhat with an increase in sulfur content in the fuel (Fig. 3a). In EI435 steel, regularity is not observed.

The results from the investigation of corrosion in the other metals tested in fuel combustion products are shown in Table 2.

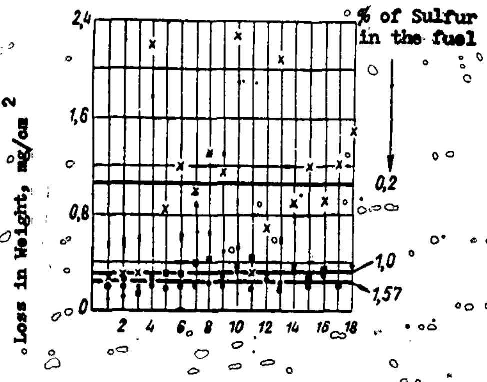

Fig. 2. Corrosion losses in 2Kh13 Steel in diesel fuel combustion products at 750°.

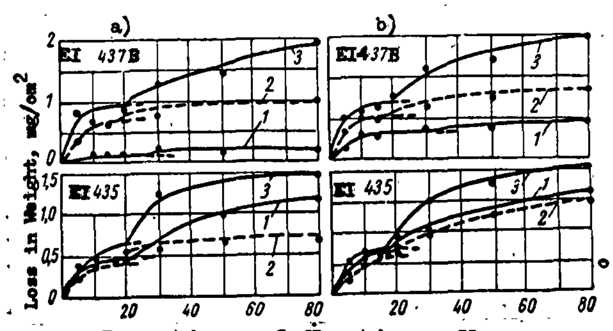

Fig. 3. Kinetics of corrosion (a) and depositions (b) in steels exposed to diesel fuel combustion products at 950°. 1) DS, GOST 4749 (0.2% S), 2) sulfur-containing fuel GOST 305-58 (1.0% S), 3) experimental sulfur-containing fuel (1.57% S).

Figure 4 shows the dependence of corrosion losses in nickel steels EI437B, EI602, and EI435 on the temperature of the combustion products of fuels containing 0.2 to 1% S. Similar "corrosion-temperature" curves were obtained for the following steels also: EI481, 3Kh13, EI417, EI612, EI607, EI617, etc.

The results show that the heat resistance of the tested steels noticeably decreases at high temperatures: for iron-base steels this phase appears at 600-700°, and for nickel steels at 750°-800°. Raising the sulfur content of the fuel from 0.2 to 1% in the 400-900° range does not essentially change the heat resistance of the given steels.

Under the working conditions of marine gas turbines, it is possible that a certain amount of sea water may get directly into the fuel or the air drawn in. Thus, the influence or water vapor on the corrosion of metals in fuel combustion products was investigated. Water containing 9 g of NaCl per liter introduced into the air igniting the fuel was mixed with it directly at the jet in the combustion area.

Corrosion of alloys by sulfur-containing fuel-combustion products in the presence of 1.0% (by fuel weight) of salt water in the air is, in the majority of cases, somewhat greater than in low-sulfur fuel. The coefficient of increase in transition to sulfur-containing fuel is within the limits of 1.2-2.0.

Decreasing the amount of salt water to 0.3% considerably diminishes corrosion losses in sulfur-containing diesel fuel, practically reducing them to the level of low-sulfur fuel.

In the operation of gas turbine the periods of work may alternate with prolonged inactivity of the equipment. Under these conditions the components of the steam-passing part of the turbine may be subjected to the action not only of fuel combustion products but also

of the moisture in the air (alternate action of combustion products and moisture).

Table 2

Corrosion of Steels (mg/cm²)						
Steel	Duration of Experiment, Hours	Temperature of Combustion Products, °C	0.2 in GOST 4749-49	1.0 in GOST 305-58	Fuel with Sulfur Content, % 1.4 — Experimental from Factory in Lyubertsy	1.5 — Novo-Kuibyshev
1Kh18N9T			0.20	0.10	0.18	—
2Kh13			0.25	—	0.15	—
3Kh13	30	550	0.20	0.21	0.15	—
EI612			0.29	—	0.29	—
10 Steel	10		2.12	—	1.71	—
EI437B			0.08	—	0.02	—
EI481	50	650	2.22	—	1.17	—
10 Steel			70.0	—	10.0	—
Nickel-Chromium (II)*	30	860	0.86	—	1.26	—
EI437B			1.20	0.69	—	1.44
EI437B			0.16	0.99	—	1.93
Nickel-Chromium (I)**	80	950	1.30	1.06	—	1.62
EI481			125.0	74.3	—	133.5

*13% Cr + 70% Ni
**(14 ÷ 17)% Cr + (68 ÷ 72) % Ni

In this connection a series of experiments was carried out to investigate the corrosive attack of sulfur-containing fuels under conditions of alternate action by combustion products and by air of ordinary humidity.

Table 3 lists the comparative data on the corrosion of steels subjected to alternate action of products of combustion with and without air moisture.

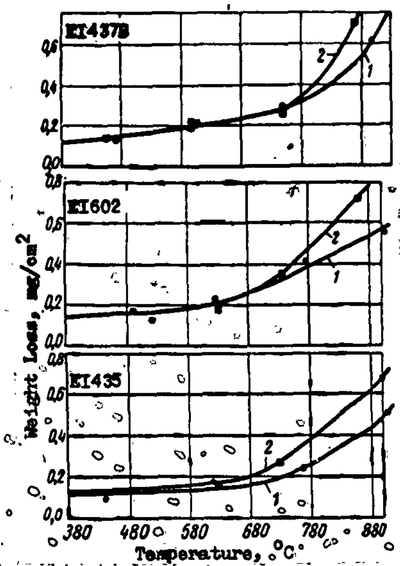

Fig. 4. Corrosion of nickel alloys in diesel fuel combustion products at different temperatures. 1) DS, GOST 4749-49 (0.2% S), 2) Sulfur-containing fuel GOST 305-58 (1.0% S).

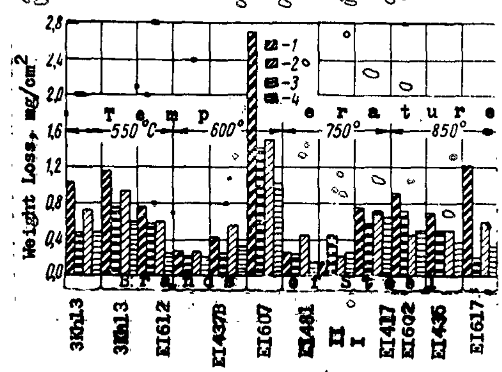

Fig. 5. Corrosion of different steels in diesel fuel combustion products after 15 hrs in the presence and absence of salt. 1) GOST 305-58 (1.0% S), 2) DS GOST 4749-49 (0.2% S), (in both cases 1% of salt water was introduced into the air); 3) GOST 305-58 (1.0% S), 4) DS, GOST 4749 (0.2% S) (in both cases without salt water).

Table 3

Corrosion (mg/cm^2) of Steels under Different Conditions. Duration of Test 30 Hours, Temperature 550°.

Steel	Fuel: Lyubertsy Works Experimental, 1.4% S — Action only of Combustion Products	Fuel: Lyubertsy Works Experimental, 1.4% S — Alternating Action of Combustion Product and Air Moisture	Fuel: GOST 305-58 1.0% S — Action only of Combustion Products	Fuel: GOST 305-58 1.0% S — Alternating Action of Combustion Product and Air Moisture	Fuel: GOST 4749-49 0.2% S — Action only of Combustion Products	Fuel: GOST 4749-49 0.2% S — Alternating Action of Combustion Product and Air Moisture
2Kh13.....	0.15	0.50	—	—	0.19	0.29
3Kh13.....	0.15	0.49	0.21	0.23	0.20	0.15
1Kh18N9T..	0.18	0.32	0.11	0.17	0.20	0.17
EI481.....	—	0.75	—	0.33	—	0.31
EI437B....	—	0.18	—	0.11	—	0.17

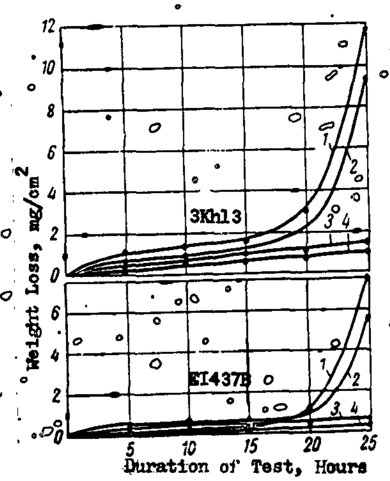

Fig. 6. Corrosion of steels in alternating action of diesel fuel combustion products and atmospheric moisture of 60 g/m^3. Sulfur-containing fuel 1) 1.57% S, 2) 1.43% S, 3) 1.0% S in GOST 305-58, 4) 0.2% S in low-sulfur fuel GOST 4749-49.

The tests were carried out in stages: after each 10-hour action of fuel combustion products the specimens were kept in air for 12 hours and thus were exposed to the effects of air moisture.

Evidently, under these conditions the corrosion of steels on an iron (EI481, 1Kh18N9T, 3Kh13, and 2Kh13) and a nickel base (EI437B) is the same as in the case where the combustion products of fuels contained 0.2 and 1.0% sulfur.

In combustion products of fuel with 1.4% sulfur, the corrosion losses of steel on an iron base (EI481) are 2-2.5 times greater than for the two other fuels; EI437B nickel steel corrodes almost identically when exposed to the combustion products of all three fuels.

Thus, in the conditions of the accepted test regime, the combustion products of fuels containing from 0.2 to 1.0% of sulfur have practically identical corrosion activity in relation to the steels on nickel and iron bases.

Increasing the sulfur content in fuel more than 1.0%, in particular to 1.4%, strengthens the corrosive action of combustion products; and this is, above all, expressed in the increase of the corrosion losses of steels on an iron base.

In addition to the described experiments, a number of others were carried out in which, owing to the artificial introduction of air of increased humidity (60 g/m^3), there was acceleration of the corrosion process.

Experiments were conducted on four fuels with various sulfur contents (0.2, 1.0, 1.4, and 1.57%).

A comparative evaluation of the corrosive attack of fuel combustion products under these conditions is given in Fig. 6.

An analysis of the data in Fig. 6 shows that the corrosive

attack of fuel combustion products in relation to iron and nickel-base steels increases out of proportion with the increase in sulfur content in the fuel; barely increasing the sulfur content, from 0.2 to 1.0%, the corrosive activity rises sharply in fuels containing 1.4-1.6% sulfur and that very fact differentiates the examined fuels into two groups according to their corrosive attack.

Analysis of the combustion products of fuel containing varying amounts of sulfur for SO_2 and SO_3, shows that the quantity of sulfur trioxide in combustion products of fuels with 0.2 to 1.0% of sulfur is almost identical; but with 1.4-1.57% of sulfur in the fuel it increases sharply. This may be the explanation of its absence in the corrosive aggressiveness of fuels containing 0.2-1.0% and 1.4-1.57% of sulfur.

Corrosion increase in alternate action of combustion products and of moisture evidently occurs because here two types of corrosion take place: chemical or gas corrosion at high temperatures and electrochemical corrosion at medium temperatures.

The possibility of electrochemical processes is inherent in the condensation of moisture and sulfuric acid on the surface of the metal.

Products of the reaction of the metal with an external medium remain on the metal in the form of incrustations. These incrustations cause wear of the turbine parts (especially of the working vanes) and unfavorably affect the operation of the gas units.

Figure 3b gives the curves for growth of incrustations plotted against time for nickel alloys exposed to sulfur-containing diesel-fuel combustion products at 950°. The quantity of incrustations is determined by comparing the weight of the specimen after the tests with its weight after electrochemical treatment: thus the incrustations contain products of corrosion, physical impurities in the stream, and

products of incomplete chemical combustion of the fuel.

From Fig. 3a and b it is to be seen that the kinetics of the growth of the incrustions and corrosion follows general laws characterized by two parabolic segments and also by the agreement of the individual sections of the curves in each segment.

The development of the given processes along parabolic segments is evidently explained by the sudden disturbance of the protective coating: the corrosion, process, sharply retarded because of protective-coating formation, accelerates anew after the destruction of the coating.

Increased sulfur content in the fuel does not disturb the general laws of corrosion and incrustation.

It was also established by experiments that the quantity of incrustations on nickel and iron alloys during the action of combustion products of fuels containing 0.2 and 1.0% of sulfur is practically identical.

On the basis of the work performed we may draw the following conclusions:

1) Tests have shown that combustion products of diesel fuels containing 0.2-1.0% sulfur possess practically the same corrosive aggressiveness in respect to steels (alloys) on a nickel and an iron base. Increasing the sulfur content in the fuel to 1.4-1.6% leads to a certain strengthening of corrosive action.

2) Combustion products of sulfur-containing fuel in a number of steels (for example, EI481 and 2Kh13 steel), when the humidity of the air entering the combustion chamber is low, may somewhat retard the corrosion process in comparison with the combustion products of low-sulfur fuel; and this evidently results from formation on the metal surface of a protective sulfide coating.

3) Alternate action of combustion products and air moisture, reflecting the concrete conditions of corrosion formation in gas

turbines, intensifies the corrosion of alloys 2-3 times when the fuel contains 1.4-1.57% of sulfur, in comparison with fuels containing 0.2-1.0% of sulfur. This is especially noticeable with increased humidity of the air.

In fuels containing 0.2-1.0% of sulfur, corrosion under such conditions is practically the same.

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